

INTERACTION OF GLASS FIBER AND HARDENED CEMENT PASTE

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The results of investigations of the interaction of hardened cement paste and glass fiber used for disperse reinforcement of concrete are presented. It is found that the character of the interaction depends on the chemical composition of the fiber, the composition of the cement, and the conditions of hardening of the concrete. It is shown that for steam-heated concretes it is more expedient to use fine-milled basaltic glass fiber instead of basaltic fiber. In this case the strength of hardened concrete paste in compression can be increased by up to a factor of 2.

Key words: disperse reinforcement, cement, glass fiber, corrosion resistance, determination of alkali-resistance.

The use of glass fiber for disperse reinforcement of concretes is considered to be an effective method of increasing the fracture resistance of concretes [1]. However, in most cases the low resistance of glass fiber to alkaline media is an impediment to wide use of this method. The appearance of an alkaline medium in the hardening concrete is due to the presence of alkali oxides and free lime in the initial cement as well as hydrolysis of calcium silicates during the hardening of the concrete mixture [2]. The adverse effect of this phenomenon is especially noticeable during steam heating of concrete dispersely reinforced by basaltic fiber.

In our previous research on the interaction of glass fiber and hardened cement paste, different experimental models of the system consisting of hardening concrete and glass fiber were used. For example, in [3] glass fiber was boiled in an alkali solution. In this case the degree of corrosion of the glass fiber was judged according to the change in its diameter. In [4] fiber was introduced into soluble beam-shaped samples during their formation and the change in strength of the samples in tension was determined as a function of the hardening time in comparison with the same samples without the fiber. It was proposed that the products of the interaction of the fiber with the alkaline medium at the interface of the media around the fiber form a shell. In addition, the adhesion of this shell to the fiber is less than to the hardened cement paste, and for this reason when the sample is stretched the fiber easily separates from the shell and does not function as a reinforcing element of the structure.

These models for studying the alkali resistance of glass fibers have a number of drawbacks. For example, when the fibers are boiled it is impossible to determine the products of the glass–fiber interaction. Similarly, in the second method, when testing small beams it is impossible to observe and investigate the changes occurring in the composition and structure of the fiber.

We have proposed a method for studying the interaction of glass fiber and hardening cement that permits observing the leaching of the fiber directly in the cement medium by using inserted samples. The advantage of this method lies in the fact that it becomes possible to track the changes in the fiber itself and to see the products of its interaction with the medium by using an electron microscope [5].

Glass fibers with different chemical compositions were used for the experiment: S5 (types S5-114, S5-117, S5-128) and basaltic fiber. The chemical composition of the fiber was determined by means of x-ray and electron spectroscopy and the degree of connectedness f_{Si} of the silicon-oxygen framework was calculated.

The degree of connectedness f_{Si} of the silicon-oxygen framework for glass and basaltic fibers is as follows:

$$S5-114 — f_{Si} = 0.278;$$

$$S5-117 — f_{Si} = 0.300;$$

$$S5-128 — f_{Si} = 0.345;$$

$$\text{basaltic fiber} — f_{Si} = 0.471.$$

Electronic photomicrographs of the fibers are displayed in Fig. 1.

Sample inserts were fabricated at the preparatory stage of the experiment; subsequently, they were inserted into the cement paste during formation. One end of the expanded fibers

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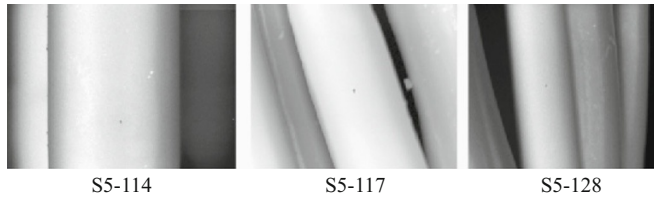


Fig. 1. Electronic photomicrographs of glass fiber before interaction with a cement medium.

was glued to a polyethylene plate of the required size in a manner so that the gluing site on formation of the samples was above the surface of the sample and not in contact with it. During formation the insert was placed with the fibers on the outside of the wall of the mold and cement paste was poured in. In this way, the fiber is in close contact with the cement paste. After the requisite hardening time and the molds were dismantled the insert was carefully separated from the cement sample. In this case part of the sample material is extracted together with the fiber and is accessible for study. The surface of the fiber with the extracted material was subjected to x-ray spectral and electron-microscopic analysis.

The fiber surface was analyzed after it interacted with the cement medium for 7, 14 and 28 days. Examination of the fiber surface under an MIN-8 optical microscope with 320-fold magnification showed that over 28 days of interaction the diameter of the fibers remained almost unchanged, while new growths with 3 – 15 μm particles appeared on the fiber surface. Since it is difficult to identify the mineral phases for crystallites of such sizes, for a more detailed analysis an x-ray spectral analysis of the surface of the extracted fiber was performed. An example of such an analysis is presented in Table 1; electron microscopic photographs of the same fibers after 28 days of contact with the hardening cement are shown in Fig. 2.

In addition, impurity quantities (from thousandths to tenths of percent) of 3d-elements, 5d-elements, and other impurities are present in all types of glass fiber.

Judging from the chemical composition, the new growths on the S5 glass are mainly calcium hydrosilicates, hydroaluminates, and hydroferrites as well as a small amount hydro-sulfoaluminates, i.e., the usual new growths, characteristic products of the solidification of cement.

The new growths have a tangled-fibrous felt-like structure.

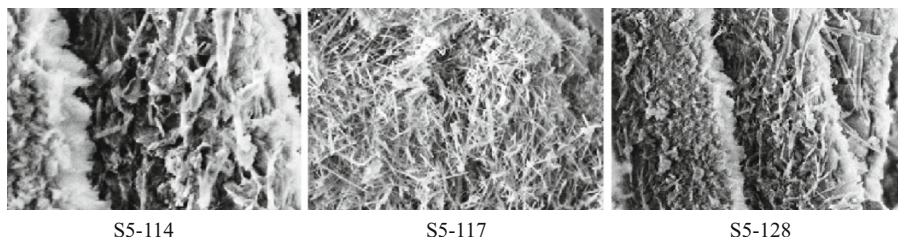


TABLE 1. Elemental Composition of Glass Fiber Before and After Contact with a Cement Medium

Element	Elemental composition of the fiber surface, wt. %			
	S5-128		basaltic	
	before contact	after 28 days	before contact	after 28 days
O	51.08	54.49	47.62	52.47
Na	0.74	—	2.45	0.68
Mg	0.87	0.78	2.88	2.65
Al	8.51	2.67	10.23	7.96
Si	21.62	8.13	21.83	2.22
K	0.33	0.41	1.32	0.32
Ca	16.85	30.20	6.13	30.37
Fe	—	1.19	6.78	1.12
S	—	2.13	—	2.21

In other photographs it is evident that the new growths can be easily separated from the surface of the fiber (Fig. 3).

An entirely different picture is observed with the same method of investigating the interaction of basaltic glass fiber with hardened Portland-cement paste with different content of alkalis (Fig. 4).

According to K. F. Paus, the energy state of the hydrate shell surrounding the particles in water dispersions prevents singly charged ions from passing through it to the surface of the particle [6]. The alkali ions cannot interact directly with particles of glass. For such an interaction the glass must first be dissolved in the solution of the alkali component. However, many experimental facts indicate that glass does not dissolve in the alkali component; one can only talk about leaching of individual components of the glass by the liquid phase [6 – 8]. Thus, a description of the mechanism of hydration of the glass in the alkali solution must be constructed assuming that no direct bonding can occur between the silicate framework of the glass and the alkali metal and the hydration must occur without the formation of the alkali compounds with the silica of the glass.

The presence in the glass of complex forming transition elements, for example, 3d- and 5d-elements, makes the formation of clusters with the participation of calcium hydrosilicates already present in the cement glue energetically favorable. In addition, hydrosilicates can play the role of monodentate or bidentate ligands. Crystallites belonging to a monoclinic system are most likely to form in the presence of

Fig. 2. Surface structure of glass fiber after contact with a cement medium for 28 days.

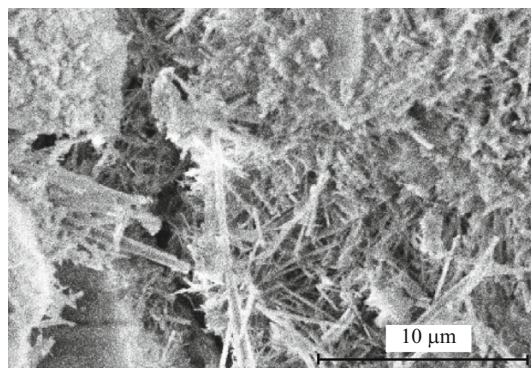


Fig. 3. Surface of a glass fiber after interaction with hardened cement paste. An easily separated shell of new growths is visible.

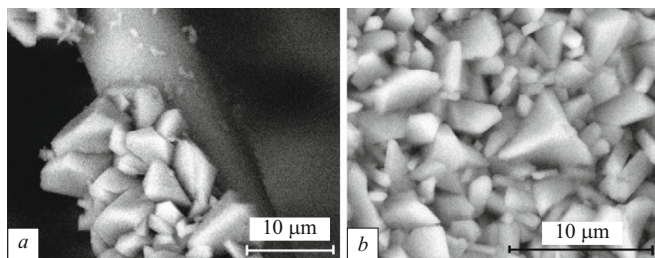


Fig. 4. Structure of new growths during contact between basaltic glass fiber and hardened cement paste: *a*) hardening under natural conditions; *b*) during steam heating.

Cu, Zn and other elements with a small number of d-electrons. In the presence of elements with a large number of d-electrons, for example, Ti, Cr and others, hydrosilicates form crystallites belonging to a triclinic system with short-prismatic pseudocubic habitus. In the case considered here, S5 and basaltic glasses contain about 20 d-elements and, apparently, the symmetry of the hydrosilicate crystals arising in the presence of the glasses studied depends on a collection of these elements and their quantitative ratio.

In all cases the new growths at the contact between the basaltic fiber and the cement are grains of size 3 – 20 μm, belonging according to the habitus to cubic and partially tetragonal systems. X-ray spectral analysis shows their composition to consist mainly of calcium hydrosilicates of the type $\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$, calcium hydroaluminates $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, calcium hydroferrite $2\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and calcium hydrosulfoaluminate $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$. However, the form of the crystallites in this case differs sharply from the well-known new growths.

Slight separation of the new growth from the surface of the glass fiber is also observed here. This attests to weak adhesion of new growth to the basaltic glass.

A dependence of the character of the new growth on the degree of connectedness of the silicon-oxygen framework is not observed in the experiment described.

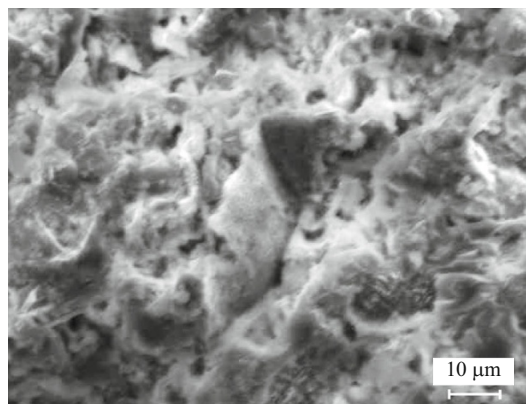


Fig. 5. The structure of hardened cement paste in the presence of milled basaltic glass fiber.

The observed character of the structure and composition of the products of interaction of the glass and the hardened cement paste shows that it is not expedient to increase the alkali-resistance of the glass fiber. The low alkali-resistance of the fiber can be used to organize the optimal structure of the hardened cement paste. To this end it makes sense to introduce finely milled glass in the form of an additive into the composition of the concrete. In this case, by adjusting the composition of the glass and the amount of glass in the composition of the concrete it is possible to form a structure of the hardened cement paste that is most favorable from the standpoint of fracture mechanics. In addition, basaltic glass is preferable from the standpoint of economics. The point is that the production of glass fiber generates waste comprised of glass but in the form of ‘straw’, i.e., rope-like formations up to 10 mm in diameter. This glass is easily ground into powder with high specific surface area comparable to that of cement.

As proof of this hypothesis we performed preliminary experiments in which wastes of basaltic glass fiber in the form of ‘straw’, subjected to milling, were used instead of basaltic fiber.

The experiments were performed as follows. Cylindrical samples in form of cylinders with diameter and height 20 mm were formed from cement paste with $F/C = 0.4$: some samples had no additives and the rest had additions of basaltic glass ranging from 5 to 15 wt.%. A part of all samples was hardened under natural conditions in 28 days. Another part of the twin-samples was steam heated in the following regime: temperature increase to 80°C — 2 h, isothermal soaking at 80°C — 6 h, and cooling to room temperature together with the chamber. The results showed that the optimal addition of the milled basaltic glass for the cements used is 9 wt.%. The microstructure of the hardened cement pastes with milled basaltic glass is shown in Fig. 5.

It was determined that under the conditions of natural hardening the strength in compression of the samples with the additive after 28 days and with steam heating for 1 day is 2 times higher after cooling compared with the control sam-

ples. The experiments showed that the use of finely milled wastes of basaltic glass fiber will make it possible to improve the properties of concretes. Basaltic glass can be introduced, for example, directly into the cement during milling. In addition, the waste in the form of unconditioned (in thickness) product from fiber production can be used.

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